

# **TOPIC 07 – EQUILIBRIUM**

## **7.2: POSITION OF EQUILIBRIUM AND LE CHATELIER'S PRINCIPLE**

IB Chemistry

T07D02



## 7.2 **7.2 The position of equilibrium - 4 hours**

- 7.2.1 Deduce the equilibrium constant expression ( $K_c$ ) from the equation for a homogeneous reaction. (3)
- 7.2.2 Deduce the extent of a reaction from the magnitude of the equilibrium constant. (3)
- 7.2.3 Apply Le Chatelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant. (2)
- 7.2.4 State and explain the effect of a catalyst on an equilibrium reaction. (3)
- 7.2.5 Apply the concepts of kinetics and equilibrium to industrial processes. (2)



# 7.1 – Summation of last class

- Dynamic Equilibrium is in a closed system, no loss or gain of material
- Amounts of reactants and products remain constant
- Dynamic, not static equilibrium. They undergo both forward and reverse reactions
- The rates of forward & reverse reactions are equal
- Equilibrium can be achieved from either direction (starting with the left or right side of the equation)
- We will study reactions in homogeneous equilibria, meaning they are all in the same physical phase.



## 7.2.1 – Equilibrium Constant ( $K_c$ )

- 7.2.1 Deduce the equilibrium constant expression ( $K_c$ ) from the equation for a homogeneous reaction. (3)
- The position of the equilibrium for a particular reversible reaction can be defined by a constant,  $K_c$
- For the general reaction:
  - $aA + bB \rightleftharpoons cC + dD$

Products on top

'powers' are coefficients

Multiple materials are multiplied

[brackets] = conc mol dm<sup>-3</sup>



## 7.2.1 – Equilibrium Law

- $K_c$  is for a given temperature, if the temperature changes then the value of  $K_c$  does as well
- The general expression of  $K_c$  is known as the **equilibrium law** which can be adapted to particular equations to be studied in equilibrium



## 7.2.1 – $K_c$ Example with Ammonia



	$[\text{N}_2] \text{ (M)}$	$[\text{H}_2] \text{ (M)}$	$[\text{NH}_3] \text{ (M)}$
Ex. 1	0.992	0.763	0.157
Ex. 2	0.299	1.197	0.203
Ex. 3	2.59	2.77	1.82

■ From Table:

▪ Find  $K_c$  for each

▪ Exp. 1

\_\_\_\_\_

▪ Exp. 2

\_\_\_\_\_

▪ Exp. 3

\_\_\_\_\_



# 7.2.1 – $K_c$ for Reversible Reactions

- For the forward reaction:



- For the reverse reaction:



- — or  $K_c^{-1}$



## 7.2.1 – $K_c$ from either side

- A series of experiments @ 700°C returns a value of  $K_c$  of 54 regardless of the starting point of reaction or initial concentrations
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

	$[\text{H}_2] (10^{-3} \text{ M})$	$[\text{I}_2] (10^{-3} \text{ M})$	$[\text{HI}] (10^{-3} \text{ M})$	$K_c$
Ex. 1	4.56	0.74	13.49	54
Ex. 2	3.56	1.25	15.50	54
Ex. 3	2.25	2.34	16.86	54

- $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

	$[\text{H}_2] (10^{-3} \text{ M})$	$[\text{I}_2] (10^{-3} \text{ M})$	$[\text{HI}] (10^{-3} \text{ M})$	$K_c'$	$K_c(1/K_c')$
Ex. 1	0.48	0.48	3.52	0.0186	54
Ex. 2	0.50	0.50	3.67	0.0186	54



## 7.2.1 - Practice

- Write the equilibrium Expression for the following reversible reactions. Each are homogeneous equilibria
  - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
  - $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons [\text{Fe}(\text{SCN})]^{2+}$
  - $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$



## 7.2.1 – Calculate reverse $K_c$

- The following reaction is an esterification reaction producing ethyl ethanoate:



- The value of  $K_c$  for this reaction is 4.0 @ 25°C
- This equilibrium can be approached from the reverse reaction, find the  $K_c$  of that reaction:



# 7.2.2 – Meaning of the Magnitude of $K_c$

- 7.2.2 Deduce the extent of a reaction from the magnitude of the equilibrium constant. (3)
- The magnitude of  $K_c$  gives us an indication of how far a reaction has gone towards completion under the given conditions
- If  $K_c$  is high = equilibrium “lies to the right”
  - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) \quad K_c = 10^{18} \text{ @ } 277^\circ\text{C}$
- If  $K_c$  is low = equilibrium “lies to the left”
  - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \quad K_c = 2 \text{ @ } 277^\circ\text{C}$
  - Bonding in HI is weaker than in HCl. HCl doesn't readily decompose in heat, where HI does.
  - Reaction to form HCl goes virtually to completion



## 7.2.2 – Relative $K_c$ values

- As a general rule:
  - If  $K_c \gg 1$  then the reaction is said to go to completion
  - If  $K_c \ll 1$  then the reaction has hardly taken place at all
  - The equilibrium constant indicates the extent of a reaction at a particular temperature.
  - It gives no indication of how fast equilibrium is achieved.

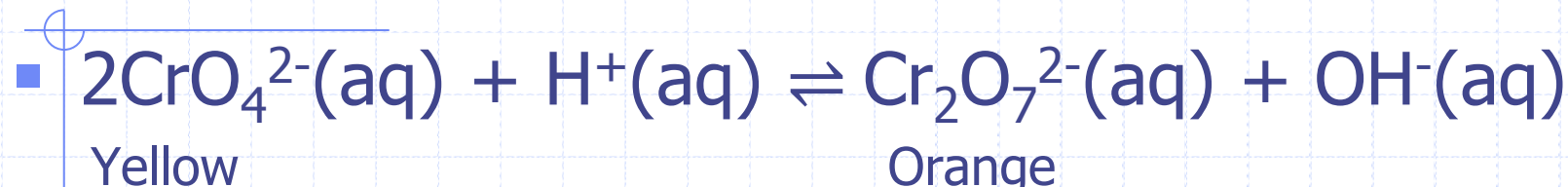
Reaction hardly goes	"Reactants" dominate at Equilibrium	Reactants equal Products	"Products" dominate at Equilibrium	Reaction virtually goes to completion
$K_c < 10^{-10}$	$K_c = 0.01$	$K_c = 1$	$K_c = 100$	$K_c > 10^{10}$

## 7.2.2 – Alterations to $K_c$

- $K_c$  is **NOT** altered by:
  - The addition of more reactants
  - The removal of some products
  - Any other adjustment
- Remember, it's the concentration, not the amount
  - If you take away 0.100L of 1.00L solution of 2.0M NaOH, you still have 2.0M NaOH left, just in less volume
- The  $K_c$  for a given reversible reaction at equilibrium only changes if the temperature changes



## 7.2.2 – Chromate and Dichromate



- The shifts are easily seen by a change in color of the ions involved
- Potassium (VI) dichromate is yellow when dissolved
  - Addition of acid pushes reaction to the left to start off at equilibrium, further  $\text{H}^+$  pushes the reaction to the right
- Potassium (VI) chromate is orange when dissolved
  - This solution favors a solution of low pH



## 7.2.3 – Le Chatelier's Principle

- 7.2.3 Apply Le Chatelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant. (2)
- **"When a system at equilibrium is disturbed, the equilibrium position will shift in the direction which tends to minimize, or counteract, the effect of disturbance."**  
-Henri Louis Le Chatelier (1850-1936)



## 7.2.3 – What does it mean?

- If conditions at which equilibrium have been established change, the position of equilibrium is effected.
- Le Chatelier's principal describes what happens when the dynamic equilibrium is disturbed but does not explain why
  - The system responds to negate the change
    - If more reactant is added, the system will react to remove it
    - If product is taken away, the system will act to replace it





## 7.2.3 – Effects on position and $K_c$

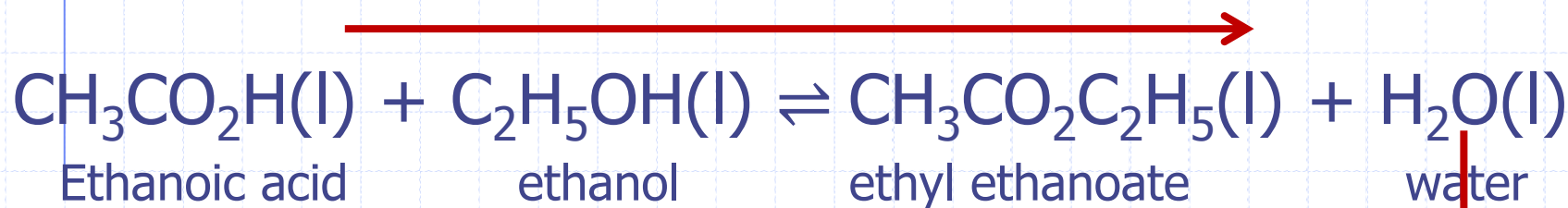
- Possible changes in conditions to consider:
  - Changes in [conc] of reactants or products
  - Changes in pressure for gas phase reactions
  - Changes in temperature
  - The presence of a catalyst

Change Made	Effect on 'position of equilibrium'	Value of $K_c$
[conc] of one of the components in the mixture	Changes	Remains unchanged
Pressure	Changes if the reaction involves a change in the total # of gas particles	Remains unchanged
Temperature	Changes	Changes
Use of a catalyst	No change	Remains unchanged

## 7.2.3 – Changes in [conc]

- Again, consider the esterification reaction:

Step 2: equilibrium is shifted to the right



Step 1: Product is removed

- If we remove water, then more of the reactants will react to replace it, producing more ester and water

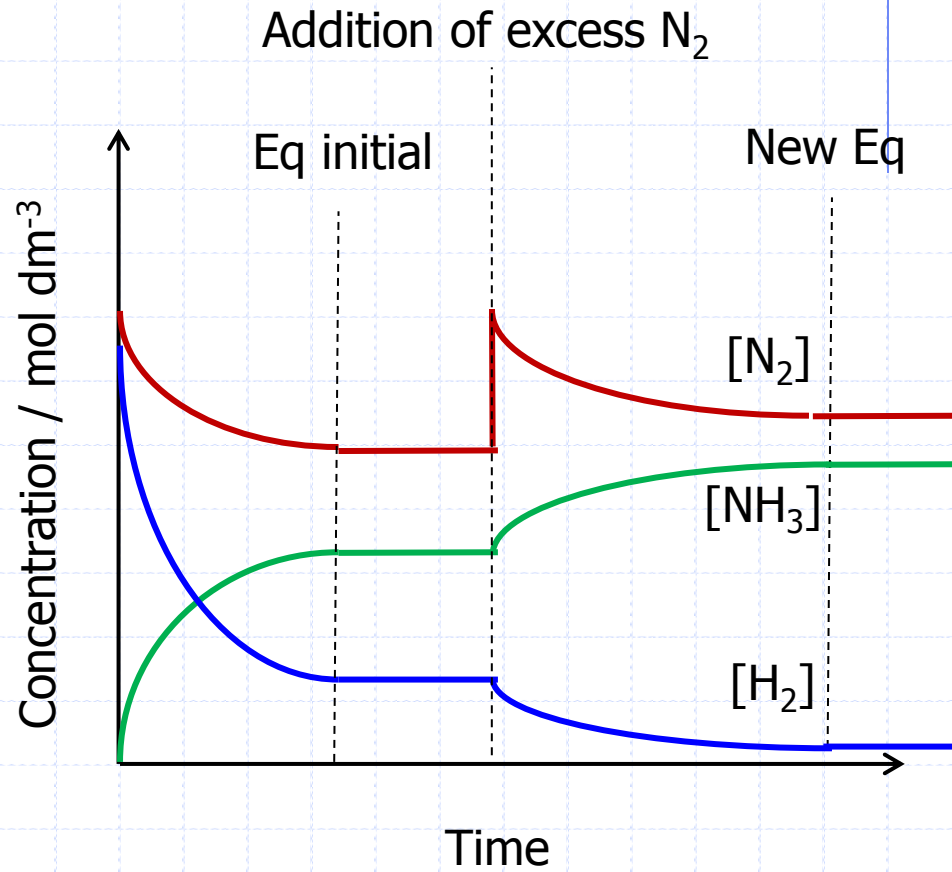
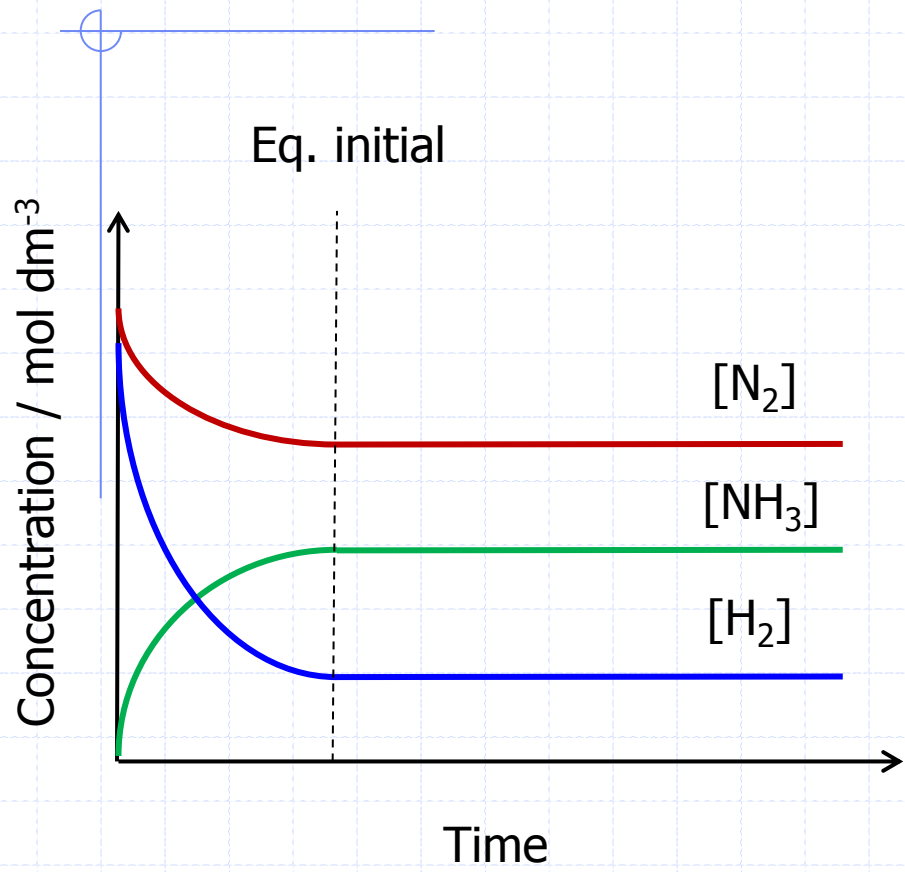


## 7.2.3 – Production of Ammonia

- A very important industrial process is the production of ammonia ( $\text{NH}_3$ )
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
  - When the reaction is in dynamic equilibrium, the concentrations are constant
  - If excess  $\text{N}_2(\text{g})$  is added, the equilibrium at first is no longer stable
  - To return to equilibrium, more  $\text{NH}_3$  is produced
  - Check out the following graphs on the next slide



# 7.2.3 – Equilibrium Shift for $\text{NH}_3$ production with addition of reactant



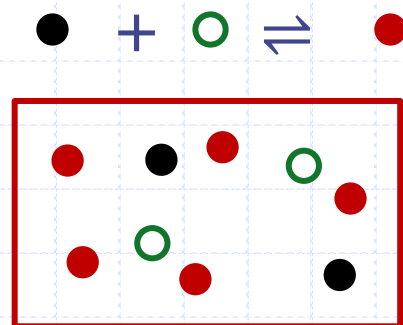
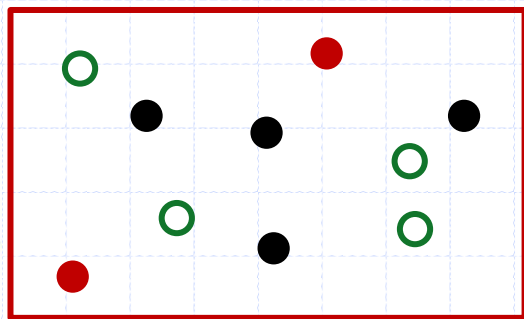
In general:

- Increasing [reactant] shifts equilibrium to the right
- Increasing [product] shifts equilibrium to the left



## 7.2.3 – Change in Pressure

- Pressure only affects gaseous reactions
- There is a direct relationship between the number of molecules of gas present and the pressure it exerts on its container
- If pressure is increased, the system will favor the side of the reaction with less molecules
  - In doing so the pressure of the mixture will be reduced



Yes, this is a change volume, but in effect it's a change in pressure



## 7.2.3 – Pressure of N<sub>2</sub>O<sub>4</sub>

- Useful reaction to study for change in pressure:



colorless

brown

- The equilibrium can easily be monitored by a change in color
- Pressure is increased:
  - Initially darkens the solution, then equilibrium shifts to the left (less molecules) and becomes lighter
- Pressure is decreased:
  - Initially lightens the solution, then equilibrium shifts to the right (more molecules) and becomes darker



This can be demonstrated with a simple syringe

## 7.2.3 – Change in Temperature

- Consider whether  $\Delta H$  of the forward reaction is positive or negative
- A reversible reaction has a enthalpy change equal and opposite for each direction (forward and reverse)
- When temperature is increased, the equilibrium position will shift in the direction that will tend to lower the temperature (endothermic direction)
- When the temperature is decreased, shifts toward the exothermic direction



## 7.2.3 – Effect of Temp on $\text{N}_2\text{O}_4(\text{g})$

- For the same reaction:



colorless

brown

$$\Delta H = + 57 \text{ kJ mol}^{-1}$$

- Decomposition is endothermic
  - If put in an ice bath, color will get lighter
  - If put in a hot water bath, color will get darker

Nature of forward reaction (sign of $\Delta H$ )	Change in temperature	Shift in the position of equilibrium	Effect on value of $K_c$
$\Delta H > 0$	Increase	To the right	$K_c$ increases
$\Delta H > 0$	Decrease	To the left	$K_c$ decreases
$\Delta H < 0$	Increase	To the left	$K_c$ decreases
$\Delta H < 0$	Decrease	To the right	$K_c$ increases



## Break – Next Class:

7.2.4 State and explain the effect of a catalyst on an equilibrium reaction. (3)

7.2.5 Apply the concepts of kinetics and equilibrium to industrial processes. (2)



## 7.2.4 – Effect of a Catalyst

- 7.2.4 State and explain the effect of a catalyst on an equilibrium reaction. (3)
- A **catalyst** is a substance that increases the rate of a chemical reaction by providing an alternative reaction pathway of lower activation energy ( $E_a$ )
- Industrially catalysts are of significance, as they allow reactions to occur at reasonable rates under milder, and therefore more economic, conditions



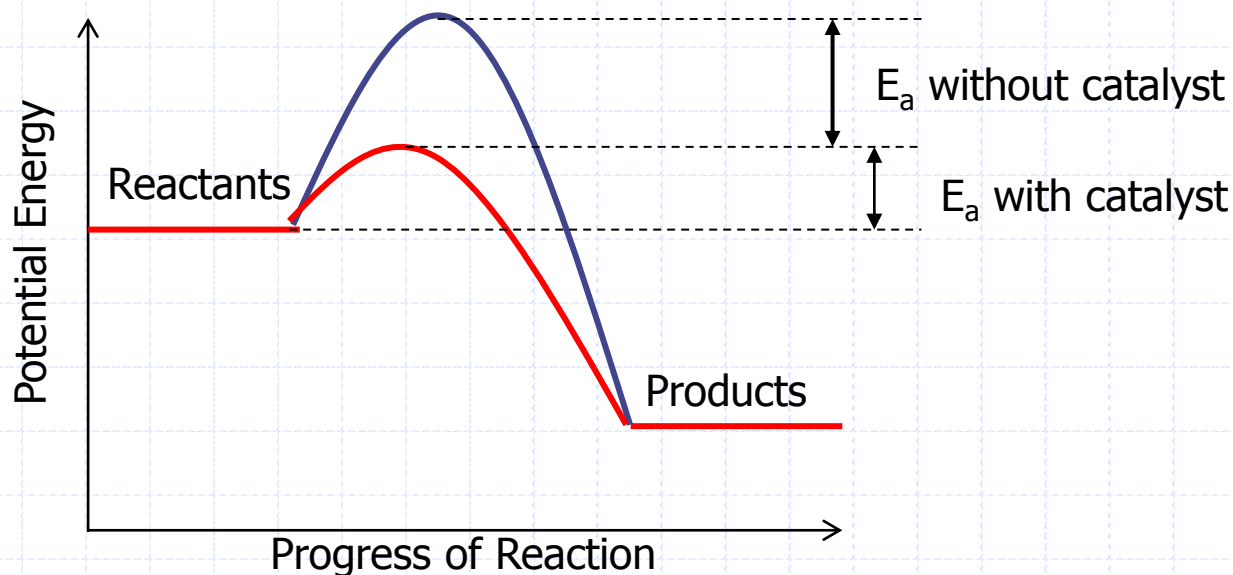
## 7.2.4 – Catalyst – $\Delta$ in equil or $K_c$

- Catalysts have no effect on the position of equilibrium
- The rates of both the forward and reverse reactions are lowered by providing an alternative pathway
- There is no change in the  $K_c$  value either
- The real advantage of a catalyst is that it reduces the time required for the equilibrium to be established.



## 7.2.4 – Catalyzed Reaction Review

- The uncatalyzed reaction of ethanoic acid and ethanol takes weeks to reach equilibrium, with the addition of hydrogen ions ( $\text{H}^+$ ), it can be reached in a few hours
- $\text{CH}_3\text{CO}_2\text{H}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$   
ethanoic acid                      ethanol                      ethyl ethanoate                      water



## 7.2.5 – Industrial Processes

- 7.2.5 Apply the concepts of kinetics and equilibrium to industrial processes. (2)
- Many very important chemicals needed in industry are formed through reversible reactions in equilibrium
- If we can take advantage of Le Chateliers Principle and manipulate the physical conditions large economic benefits may result.
- The rate at which product is produced is also of economic concern.



You will study the **Haber** and **Contact** Processes

## 7.2.5 – Haber Process for Ammonia

- Nitrogen is of extreme importance for plant growth
- Most plants cannot 'fix' nitrogen directly from air (which is 78%  $\text{N}_2$ )
- Only certain plants can convert nitrogen directly into a usable chemical with use of a bacteria present in their root nodules
- To promote plant growth – N-compounds are added to crops as fertilizers (All use  $\text{NH}_3$ )

- **Urea** –  $\text{CO}(\text{NH}_2)_2$



- **Ammonium sulfate** –  $(\text{NH}_4)_2\text{SO}_4$

- **Dihydrogen phosphate** –  $\text{NH}_4\text{H}_2\text{PO}_4$

## 7.2.5 – Haber Process

- Most plants use CH<sub>4</sub> (natural gas), air, and water as starting materials.
- If CH<sub>4</sub> contains S, it will effect Ni catalyst, so removed
$$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \quad \Delta H = +206 \text{ kJ mol}^{-1}$$
  - **Ni** catalyst used at 750°C in '**primary reformer**'
- The unwanted CO(g) formed is removed from the mixture in the '**shift reactor**' by reaction with steam
- N<sub>2</sub> from the air is used but must be concentrated
  - O<sub>2</sub>(g) (20% in air) is removed in the '**secondary reformer**'



Now, for the production of ammonia:



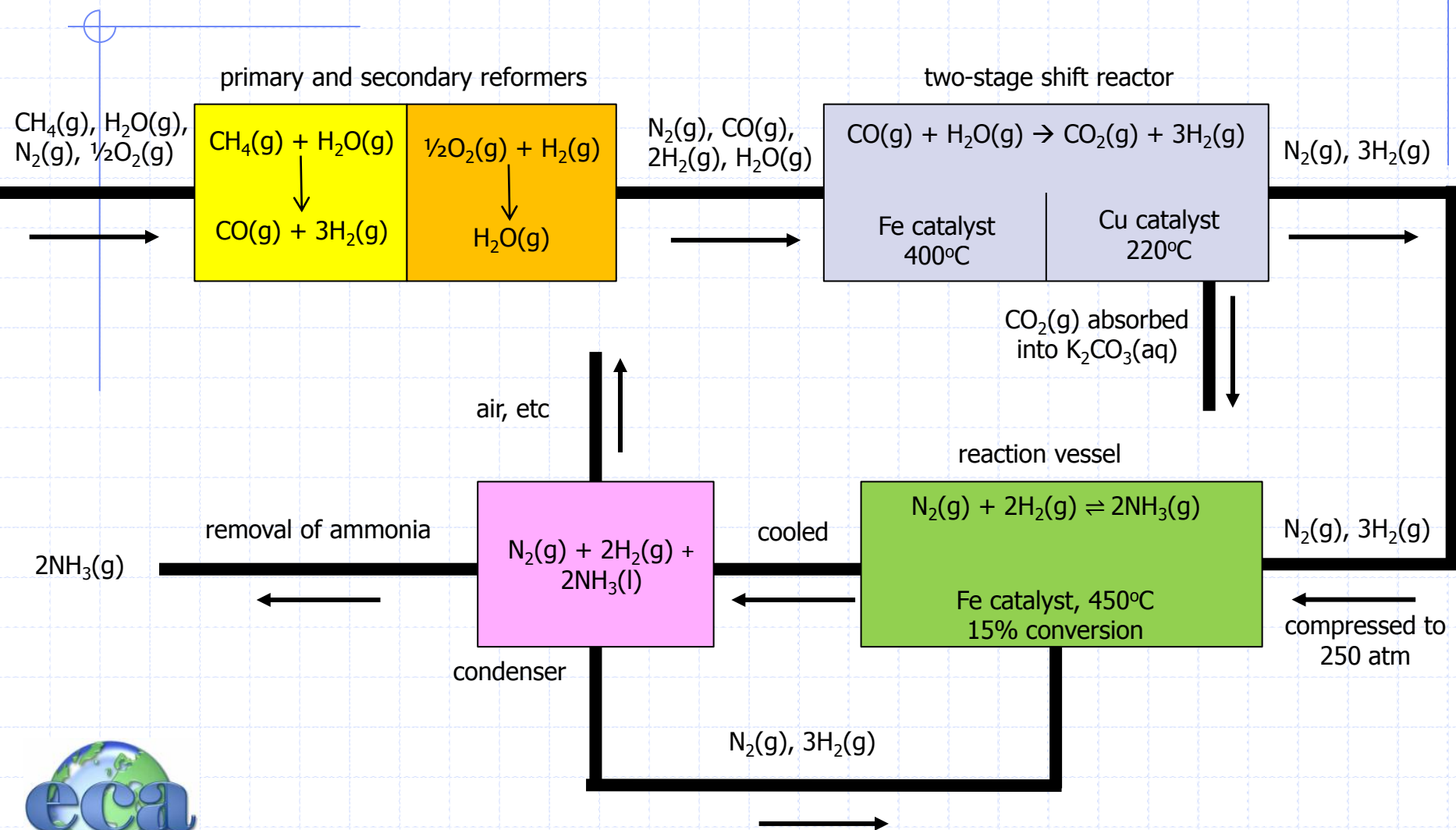
## 7.2.5 – Materials:

- So what needed?
  - $\text{CH}_4$  (Sulfur removed)
  - Steam
  - Ni (as catalyst for  $\text{CH}_4$  and  $\text{H}_2\text{O}$ )
  - $\text{N}_2$  from air ( $\text{O}_2$  removed from mixture)
- What must be removed?
  - S from  $\text{CH}_4$
  - $\text{O}_2$  from air
  - CO from products of primary reformer





# 7.2.5 – Haber Process Diagram



## 7.2.5 – Haber Process Conditions

- The conditions used in the Haber process are set using the Principles of Le Chatelier to achieve a satisfactory yield of ammonia at a reasonably economic rate



- The highest yield is produced using
  - High pressures (favors less molecules)
  - Low temperatures (favors exothermic reaction)

- But, economically, it's better to increase the rate



High temperature, high pressure, in the presence of a catalyst

## 7.2.5 – Haber Choice of Pressure

- For reasons discussed in 7.2.3, the choice of a high pressure will favor the side of equilibrium containing less moles of gas
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \mathbf{2\text{NH}_3(\text{g})}$      $\Delta H = -92 \text{ kJ mol}^{-1}$
  - 4 moles in reactants vs. 2 moles in products
- Also favored for kinetic reasons and most industrial plants operate at 200-250 atm's (some +1000 atm)
  - Higher pressure reaction vessels are very expensive as special chromium steel is used
- The decision is made by balancing the high initial costs against eventual profit of increased yield



## 7.2.5 – Haber Choice of Temperature

- The process is exothermic, so lowering the temperature would favor the products:
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -92 \text{ kJ mol}^{-1}$
- By raising the temperature, you would assume it would result in less ammonia in the equilibrium mixture
- There are three reasons why temperature is raised:
  - Low temp = slow reaction
  - The catalyst used has an optimum operating temperature
- Ammonia can be condensed,  $\text{N}_2$  and  $\text{H}_2$  reused and not wasted, so low yield is a small concern



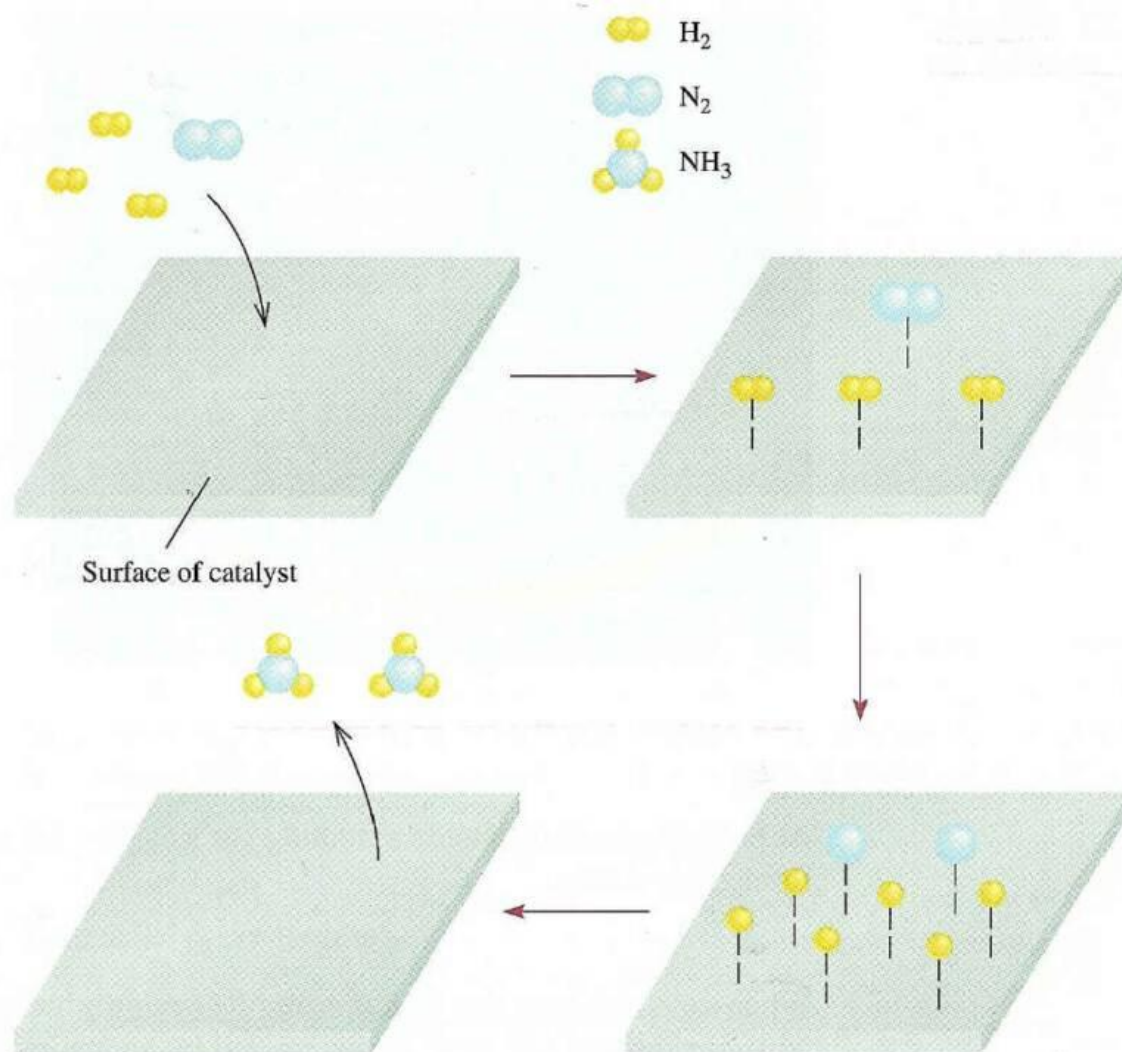
## 7.2.5 – Haber, use of catalyst

- Uses a catalyst of freshly produced, finely divided iron
  - Produced by reduction from  $\text{Fe}_3\text{O}_4$  (magnetite)
  - Used because it reduces the time to reach equilibrium
- A promoter (which improves the performance of a catalyst) is often used: molybdenum, potassium oxide, aluminum oxide, potassium hydroxide
- A typical industrial plant operates at 250 atm and 450°C and produces a conversion to ammonia of about 15%. Ammonia can be removed and the process continues.

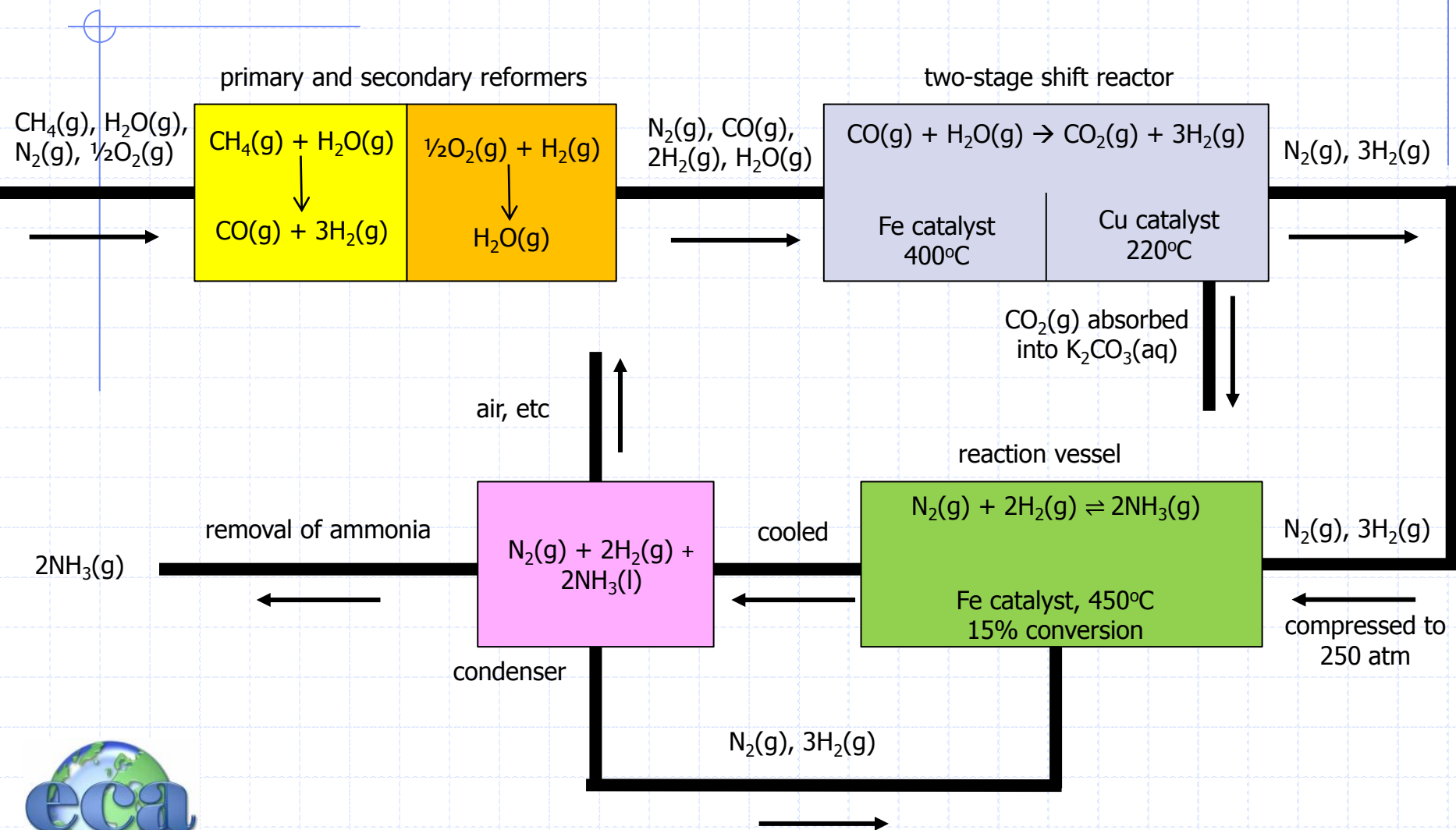


## 7.2.5 – Haber Mechanism on Iron

Through the mechanism of chemisorption,  $\text{N}_2$  and  $\text{H}_2$  molecules dissociate into their ions on the iron surface, speeding up the reaction



# 7.2.5 – Haber Process Diagram





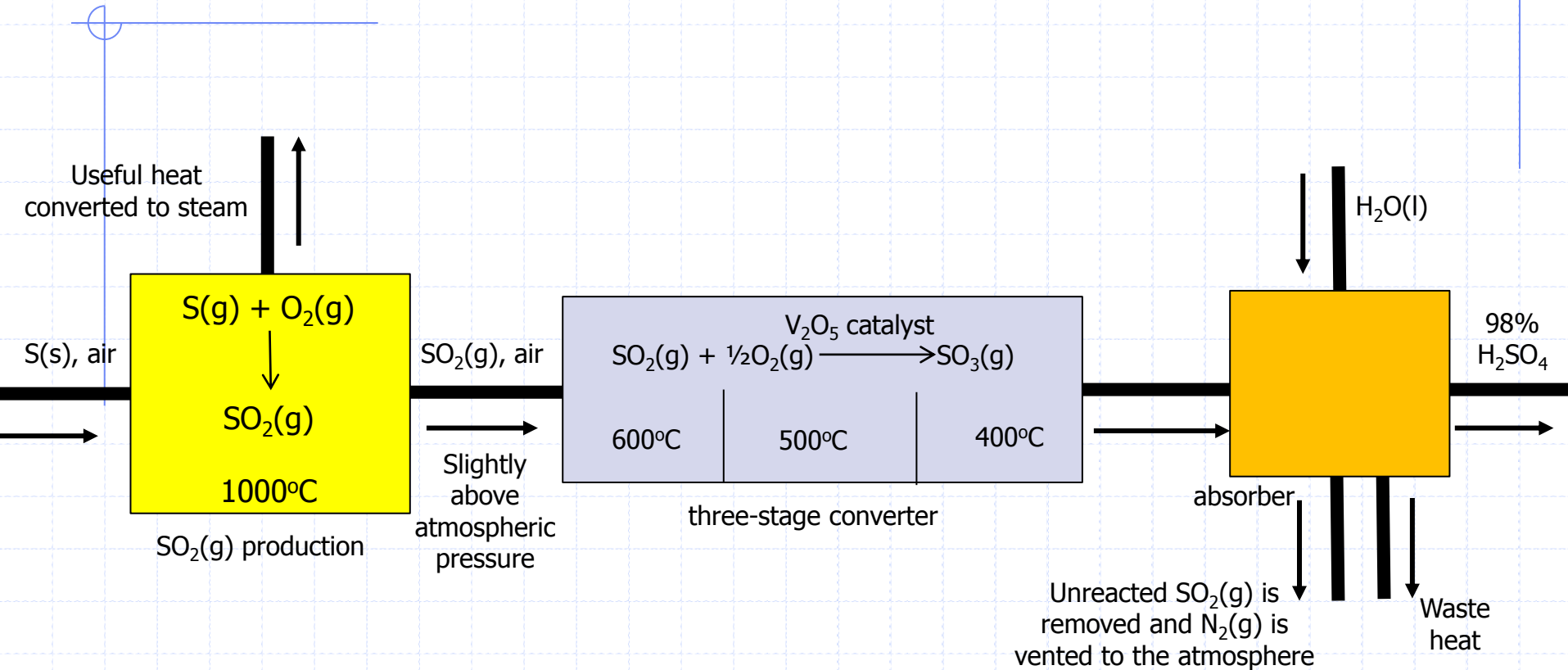
## 7.2.5 – Contact Process for $\text{H}_2\text{SO}_4$

- Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is the single most produced chemical world-wide and is produced through the contact process.
- 150,000,000 tons are manufactured each year for:
  - Fertilizers
  - Paints and pigments
  - Detergents and soaps
  - Dyestuffs
- There are three stages to the contact process





# 7.2.5 – Contact Process Diagram



## 7.2.5 – Contact Process State 1

- Sulfur is burned in air at 1000°C
  - $\text{S(s)} + \text{O}_2\text{(g)} \rightarrow \text{SO}_2\text{(g)}$



## 7.2.5 – Contact Process Stage 2

- Sulfur dioxide produced is then mixed with more air and passed over vanadium (V) oxide,  $V_2O_5$  at  $450^\circ\text{C}$ 
  - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H = -197 \text{ kJ mol}^{-1}$
- This step is known as the **Contact Step** and is reversible (in equilibrium)
- Shifted to the right by the addition of an excess of air – about 3x what is necessary
- Le Chateliers Principle suggests the highest yield of products would be at high pressure, low temperature
  - Once again, low temps = slow rates



The catalyst is only useful above  $400^\circ\text{C}$

## 7.2.5 – Contact Pressure Continued

- Therefor a starting temperature of 450°C is used for each bed, but the exothermic process raises that temperature several hundred degrees
- So, the gases are cooled back down to 450°C before passage onto the next bed
- This conversion produces a 99.5% conversion from  $\text{SO}_2$  to  $\text{SO}_3$
- Given the high rate of conversion (and cost of raising pressure) the reaction is run at 1-2 atm



## 7.2.5 – Contact Process Stage 3

- Finally, the  $\text{SO}_3$  produced is dissolved in 98% sulfuric acid and water is added
  - This is done to avoid the potentially violent and highly exothermic reaction if the gas was directly passed into water
- $\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})$
- $\text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{H}_2\text{SO}_4(\text{aq})$

